

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 628 582 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
28.03.2001 Bulletin 2001/13

(51) Int Cl.7: C08G 18/28, C08G 18/62,
C08G 18/78

(21) Application number: 94303887.7

(22) Date of filing: 27.05.1994

(54) A crosslinker and a method of crosslinking a coating binder polymer

Vernetzer und Verfahren zur Vernetzung eines Beschichtungsbindemittelpolymers --

Réticulant et procédé pour réticuler un polymère liant de revêtement

(84) Designated Contracting States:
DE ES FR GB IT NL SE

(30) Priority: 11.06.1993 US 75448
29.04.1994 US 235585

(43) Date of publication of application:
14.12.1994 Bulletin 1994/50

(73) Proprietor: ROHM AND HAAS COMPANY
Philadelphia, Pennsylvania 19106-2399 (US)

(72) Inventors:
• Brown, Ward Thomas
North Wales, PA 19454 (US)
• Day, James Clarence,
English Village Apartments
North Wales, PA 19454 (US)

(74) Representative: Tanner, James Percival et al
ROHM AND HAAS (UK) LTD.
European Operations Patent Department
Lennig House
2 Mason's Avenue
Croydon CR9 3NB (GB)

(56) References cited:
EP-A- 0 198 343 EP-A- 0 231 509
EP-A- 0 449 143 EP-A- 0 507 407
DE-A- 1 544 970 US-A- 3 267 137
US-A- 4 612 054

Remarks:

The file contains technical information submitted
after the application was filed and not included in this
specification

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 628 582 B1

Description

[0001] The present invention concerns a crosslinker and a method of cross-linking a coating binder polymer having at least two carboxylic acid groups.

5 [0002] The process of film formation is fairly well understood in the coatings industry and details on the process may be found in "Organic Film Formers" in Paint and Surface Coatings, by J. Bentley (R. Lambourne (Editor), John Wiley and Sons, New York, N.Y., 1987). In particular, in film formation technology, it is known that the addition of a cross-linker to a film forming coating formulation can improve certain important properties of the formed coating, such as its hardness, solvent resistance and mar resistance. However, it is desirable to have a cross-linking mechanism which is operative during or after film formation. If the cross-linking mechanism has proceeded materially before film formation has been substantially completed, the overall film formation process will be compromised and the resultant film will be weak and porous with the result that the protective functions of the film will be severely impaired. In some applications heat may be used to assist cross-linking after film formation is complete. However, in many cases, heat is not available so the cross-linking mechanism is desirably triggered under ambient conditions before film formation is complete.

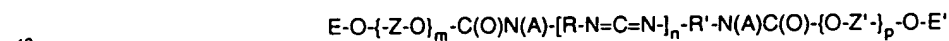
15 [0003] An example of a known good performance cross-linker for coating formulations is a product sold under the trade name of XAMA-7 (supplied by EIT Inc). XAMA-7 essentially consists of three connected aziridine groups. While XAMA-7 displays good cross-linking performance it does suffer from an important drawback. It is very toxic. It therefore has to be handled with the utmost of care. This is clearly undesirable.

20 [0004] However, not all commercial cross-linkers are as toxic as the aziridine based products. For example, carbodiimides having the general structural formula of $R-N=C=N-R'$, wherein at least R' is an aliphatic group, have been used as cross-linkers. In this regard, US-A-4977219, EP-A-0277361 and EP-A-0241805 disclose aliphatic polycarbodiimide cross-linkers, wherein both R and R' are aliphatic groups. EP-A-0277361 discloses a mixed aliphatic and aromatic polycarbodiimide cross-linker, wherein R is an aromatic group and R' is an aliphatic group. Even though these aliphatic polycarbodiimide cross-linkers are used commercially, they do suffer from certain drawbacks. In particular, cross-linking is too facile with the result that the cross-linking mechanism is substantially completed before film formation is completed. Therefore, despite the fact that a rapid cross-linking step will generally lead to an increase in cross-link density and possibly to improvements in solvent resistance, it detracts from the process of film formation. For example, there is a decrease in the important property of mar resistance. The rapid cross-linking therefore leads to the formation of generally poor and brittle coatings as they are not well-knitted.

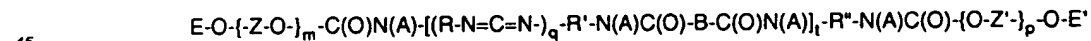
25 [0005] EP-A-0198343 discloses certain aromatic polycarbodiimides, an essential feature of which are sulfonate groups, but does not disclose the desirability of or the method by which the confounding effect of the sulphonated groups may be eliminated.

30 [0006] The present invention seeks to overcome the problems associated with the prior art cross-linkers. In particular, the present invention seeks to provide a relatively non-toxic cross-linker having a good performance in coatings, in particular aqueous coatings.

35 [0007] According to a first aspect of the present invention there is provided an aromatic polycarbodiimide having the general formula of either



or



wherein m is an integer of from 1 to 15; n is an integer of from 2 to 15; p is an integer of from 1 to 15; q is an integer of from 1 to 15; t is an integer of from 1 to 15; A is independently selected from hydrogen or C1-C6; B being an ether or ester spacer group which does not contain carbodiimide groups; E and E' are hydrogen or C1-C10 alkyl and may be the same or different; R , R' and R'' are independently selected from arylene, substituted arylene, biarylene alkylene and substituted biarylene alkylene; and Z and Z' C1-C6 alkylene groups and may be the same or different; and wherein the aromatic polycarbodiimide does not contain a chemically incorporated sulfonate group.

50 [0008] According to a second aspect of the present invention there is provided a method of crosslinking a coating binder polymer bearing at least two carboxylic acid groups, the method comprising admixing the above aromatic polycarbodiimide with the coating binder polymer.

55 [0009] The coating binder polymer is preferably a film-forming coating formulation. Film forming coating formulations include paints, sealants, nonwoven fabric binders, leather coatings, and adhesives.

[0010] According to a third aspect of the invention, there is provided an aqueous dispersion of an aromatic polycar-

bodiimide of the first aspect of the invention.

[0011] According to a fourth aspect of the present invention there is provided a water dispersible, polyether-terminated aromatic polycarbodiimide.

[0012] According to a fifth aspect of the present invention there is provided a process for preparing an aromatic polycarbodiimide as defined in any one of the preceding claims comprising reacting an aromatic isocyanate, preferably a polyisocyanate more preferably an aromatic diisocyanate, which may be the same or different, with a suitable reactant to form the aromatic polycarbodiimide.

[0013] An advantage of the present invention is that the aromatic polycarbodiimides are relatively non-toxic.

[0014] A further advantage is that the cross-linking process is much slower than that of the prior art aliphatic carbodiimide systems. It is believed that the cross-linking process may be approximately fifty times slower. The cross-linking process is slow enough for substantially all of it to occur during or after film formation with the result that a number of important requirements for a good coating, such as mar resistance, are greatly improved. The crosslinking is also fast enough to be useful in an ambiently cured film in a typical industrial or architectural use.

[0015] Further advantages of the present invention are that the water solubility of the aromatic polycarbodiimides can be tailored to suit individual needs, for example by incorporating surfactant groups. Also, the compatibility of the aromatic polycarbodiimides with specific polymer (or resin) systems can be tailored to suit individual needs, for example by incorporating suitable compatibilising groups. For example, pendent or terminal phenyl groups make the aromatic polycarbodiimides suitable for use with polyester based polymers; whereas pendant or terminal polyether groups make the aromatic polycarbodiimides suitable for use with acrylic polymers.

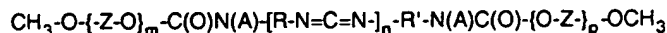
[0016] The present invention therefore rests in the discovery and recognition of a new use of aromatic polycarbodiimides as well as in the preparation of new aromatic polycarbodiimides. In this regard, even though certain aromatic polycarbodiimides (i.e. wherein both r and r' of $r-N=C=N-r'$ are aromatic groups) are known from publications such as US-A-5126422, EP-B-0231509, US-A-3450562, and US-A-2941983, none of them falls within the scope of the present invention. Moreover, none of those documents specifically suggests or reports the use of aromatic polycarbodiimides as cross-linkers. The same is true for US-A-4612054 which discloses carbodiimide driers for resin coating compositions. Whilst the general formula presented for the polycarbodiimide could cover an aromatic polycarbodiimide, there is no specific mention of, let alone a technical teaching for, both the use of the aromatic polycarbodiimides as cross-linkers and an aromatic polycarbodiimide according to the present invention.

[0017] The aromatic polycarbodiimide according to the present invention is water-soluble or readily emulsifiable in the presence of water. In particular, the aromatic polycarbodiimide is very effective as a cross-linking agent for carboxyl-containing, water borne polymers or resins (e.g. emulsion-polymerized acrylic polymer). The carboxyl-containing polymers may be totally or partially neutralised with a suitable base. The polycarbodiimide is also an effective cross-linking agent for other polymers based on epoxides, polyesters, and polyurethanes. In theory, the aromatic polycarbodiimides according to the present invention may be used as a cross-linker in any water-borne or solvent-borne thermoset coating application.

[0018] Preferably, in the method of this invention, the aromatic polycarbodiimide includes at least one substituted arylene group, preferably being derived from an aromatic polyisocyanate.

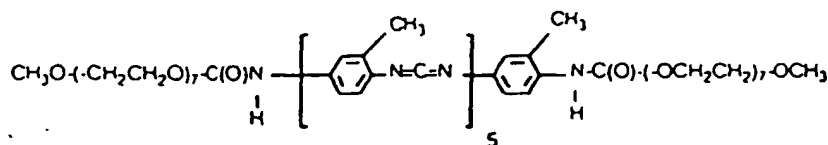
[0019] Preferably, in the method of this invention, the aromatic polycarbodiimide has from 4 to 10 aromatic carbodiimide groups, preferably 5 to 7 groups. More preferably, the aromatic polycarbodiimide has 7 carbodiimide groups.

[0020] Preferably the aromatic polycarbodiimide has the following formula



wherein m is 7; n is 7; p is 7; A is hydrogen; R and R' are substituted arylene; and Z is CH_2CH_2 .

[0021] The aromatic polycarbodiimide may therefore have the following formula



[0022] Another aromatic polycarbodiimide according to the present invention has the following formula



15

20

25

37

45

50

54

[0032] The following examples are intended to illustrate aromatic polycarbodiimides and coatings containing the same to which this invention is directed. They are not intended to limit the invention as other applications of the invention will be obvious to those of ordinary skill in the art.

EXAMPLE A PREPARATION OF AROMATIC POLYCARBODIIMIDES**EXAMPLE A1. Preparation of an aromatic polycarbodiimide with terminal phenyl groups ("PCD7")**

5 [0033] Into a round bottomed flask equipped with a heating mantle, stirrer, thermometer, condenser and nitrogen sparge were placed 9.39 g phenyl isocyanate, 20.61 g toluene diisocyanate, 27.0 g amyl acetate and 3.0 g of a 10% solution by weight of 3-methyl-1-phenyl-2-phospholene-1-oxide in xylene. The mixture was heated to 140°C. for 0.5 hours, then cooled. The resulting crosslinker was 43.3% solids with an average theoretical functionality of 4.

10 **EXAMPLE A2. Preparation of an aromatic polycarbodiimide with terminal groups derived from diethyl-3-hydroxyglutarate ("PCD6")**

[0034] Into the apparatus of Example A1 were placed 21.1 g toluene diisocyanate and 8.2 g of diethyl-3-hydroxyglutarate. The mixture was heated to 75°C. for 7 hours, then cooled. 25.0 g of amyl acetate and 1.06 g of a 16% by weight solution of 3-methyl-1-phenyl-2-phospholene-1-oxide in xylene were added. The mixture was heated to 60°C. for 6 hours, then to 80°C. for an additional 2 hours, then cooled.

[0035] The resulting cross-linker was 50% solids with a theoretical average functionality of 5.

20 **EXAMPLE A3. Preparation of an aromatic polycarbodiimide having methylether terminated polyethylene oxide end groups derived from Carbowax MPEG 350 ("PCD0")**

[0036] Toluene 2,4-diisocyanate (17.1 g, 0.098 moles) was treated with the poly(ethylene glycol) monoethyl ether Carbowax 350 (supplied by Union Carbide) (Carbowax 350, 11.5 g, 0.033 moles, mole ratio diisocyanate/Carbowax = 3/1) in a 100 ml round bottomed flask equipped with a thermometer, magnetic stirrer and a condenser with an attached bubbler. The mixture was stirred and heated to 75°C. for 1 hour to complete the alcohol-isocyanate reaction. The mixture was then cooled and 25 g amyl acetate solvent was added, followed by 0.83 g of a 16% wt solution of 3-methyl-1-phenyl-2-phospholene-1-oxide catalyst in xylene (0.133 g of catalyst, 0.7 mole % on diisocyanate). The mixture was stirred and heated to 60°C. for 2 hours and then 80°C. for 4.5 hours. The progress of the reaction was followed by loss in weight due to carbon dioxide evolution. The reaction was judged complete when the observed weight loss matched the calculated value. The product contained 50% solids in amyl acetate.

[0037] The calculated average number of carbodiimide linkages per polycarbodiimide chain is five.

35 **EXAMPLE A4. Use of hindered phenol stabilizer with an aromatic polycarbodiimide having methylether terminated polyethylene oxide end groups derived from Carbowax MPEG 350**

[0038] Toluene 2,4-diisocyanate (79.3 g, 0.456 moles) and poly(ethylene glycol) monoethyl ether Carbowax 350 (supplied by Union Carbide) (Carbowax 350, 38.5 g, 0.11 moles) was stirred and heated to 75°C. for 1 hour. 100 g. propylene glycol methyl ether acetate was added, followed by 6.1 g of a 10% wt solution of 3-methyl-1-phenyl-2-phospholene-1-oxide catalyst in xylene. The mixture was stirred and heated to 120°C. for 2 hours, during which time 17.6 g. loss in weight occurred due to carbon dioxide evolution. A 5 g. sample of final product was placed in a sealed vial in a 70 C. oven and checked periodically; after 3 days the mixture had gelled to a clear immobile mass.

[0039] Toluene 2,4-diisocyanate (19.8 g, 0.114 moles), poly(ethylene glycol) monoethyl ether Carbowax 350 (supplied by Union Carbide) (Carbowax 350, 9.6 g, 0.027 moles) and 0.05 g. (1000 ppm. based on the weight of final product) hindered phenol (IRGANOX 1010) was stirred and heated to 75°C. for 1 hour. 25 g. propylene glycol methyl ether acetate was added, followed by 1.53 g of a 10% wt solution of 3-methyl-1-phenyl-2-phospholene-1-oxide catalyst in xylene. The mixture was stirred and heated to 120°C. for 2 hours, during which time 4.4 g. loss in weight occurred due to carbon dioxide evolution. A 5 g. sample of final product was placed in a sealed vial in a 70 C. oven and checked periodically; after 6 days the mixture had gelled to a clear immobile mass.

[0040] Hindered phenol stabilizer prolonged the useful life of an aromatic polycarbodiimide of this invention.

50 **EXAMPLE A5. Preparation of an aromatic polycarbodiimide having methylether terminated polyethylene oxide end groups derived from Carbowax MPEG 350**

55 [0041] Toluene 2,4-diisocyanate (205.2 g, 1.179 moles) was treated with poly(ethylene glycol) monoethyl ether Carbowax 350 (supplied by Union Carbide) (Carbowax 350, 138.0 g, 0.394 moles, mole ratio diisocyanate/Carbowax = 3/1) in a 1 liter round bottomed flask equipped with a thermometer, magnetic stirrer, condenser, and attached wet test meter. The mixture was stirred and heated to 75°C. for 1 hour to complete the alcohol-isocyanate reaction. The mixture was then cooled and 300 g propylene glycol methyl ether acetate was added. A 20 cc./min. nitrogen sparge through

the reactor contents was then established and the mixture heated to 120 C. At 120 C., 4.44 g of a 10% wt solution of 3-methyl-1-phenyl-2-phospholene-1-oxide catalyst in xylene (0.44 g of catalyst, 0.175 mole % on diisocyanate) was added via a dropping funnel. After an initial exotherm, the mixture was stirred for 2 hours at 120 C. The progress of the reaction was followed by observing the volume of carbon dioxide evolved, obtained from the wet test meter reading after correction for the amount of nitrogen sparged. The product contained 50% solids in propylene glycol methyl ether acetate. The calculated average number of carbodiimide linkages per polycarbodiimide chain is five.

EXAMPLE B PREPARATION OF COATING SAMPLES

[0042] The following series of coating samples according to the present invention were prepared.

REF	RESIN	AROMATIC POLYCARBODIIMIDE CROSS-LINKER
IA.1	Crylcoat 2680	PCD7
IA.2	Styrene/acrylic resin; Acid No.=65.1	PCD6
IA.3	Styrene/acrylic polymer; Acid No.=97.7	PCD0
IA.4	Styrene/acrylic polymer; Acid No.=48.8	PCD0
IA.5	Styrene/acrylic polymer; Acid No.=32.6	PCD0

[0043] The following series of control samples were prepared:

REF	RESIN	ALIPHATIC POLYCARBODIIMIDE CROSS-LINKER
CP.1	Crylcoat 2680	Ucarlnk XL-20
CP.2	Styrene/acrylic resin; Acid No.=65.1	Ucarlnk XL-27HS
CP.3	-	-
CP.4	Styrene/acrylic polymer; Acid No.=48.8	Ucarlnk-25SE
CP.5	-	-

REF	RESIN	AZIRIDINE CROSS-LINKER
CA.1	Crylcoat 2680	XAMA-7
CA.2	Styrene/acrylic resin; Acid No.=65.1	XAMA-7
CA.3	Styrene/acrylic polymer; Acid No.=97.7	XAMA-7
CA.4	Styrene/acrylic polymer; Acid No.=48.8	XAMA-7
CA.5	-	-

[0044] As a final series of controls the above resins were tested without the presence of any cross-linker. These further control samples are listed as follows:

REF	RESIN
CC.1	Crylcoat 2680
CC.2	Styrene/acrylic resin; Acid No.=65.1
CC.3	Styrene/acrylic polymer; Acid No.=97.7
CC.4	Styrene/acrylic polymer; Acid No.=48.8
CC.5	Acrylic emulsion polymer; Acid No.=32.6

(Crylcoat 2680 (CC.1) is an aromatic polyester (solid) supplied by UCB with an Acid No.=50.8. CC.2 is a solvent-borne polymer; CC.3 is a dispersion of polymer in water; CC.4 is an emulsion-polymerized polymer; CC.5 is an acrylic emulsion polymer. Ucarlnk XL-20, XL-27HS and XL-25SE are all aliphatic polycarbodiimides and are supplied by Union Carbide. XAMA-7 is supplied by EIT Inc.)

[0045] These coating samples were formulated as follows. Generally, the order of mixing went from left to right (the quantities are given in grams.)

EP 0 628 582 B1

REF	RESIN	N-METHYL PYRROLIDONE	PCD7	UCARLNK XL-20	XAMA-50% IN PM ACETATE
CC.1	.625	1.875	.21	.20	.17
IA.1	.625	1.875			
CP.1	.625	1.875			
CA.1	.625	1.875			

REF	RESIN	BUTYL CELLOSOLVE	TOLUENE	PCD6	UCARLNK XL-27HS 66.7% IN PM ACETATE	XAMA-7 50% IN PM ACETATE
CC.2	1.35	.14	1.01	.43	.39	.26
IA.2	1.35	.14	1.01			
CP.2	1.35	.14	1.01			
CA.2	1.35	.14	1.01			

REF	RESIN	WATER	14% NH3	PCD0	XAMA-7 (50% IN PM ACETATE)
CC.3	7.0	2.7	.30	2.68	1.32
IA.3	7.0	4.7	.30		
CA.3	7.0	2.7	.30		

REF	RESIN	H ₂ O	14%NH ₃	BUTYL CELLOSOLVE	BUTYL CARBITOL	PCD0	UCARLNK 25SEIN	XAMA7 (50 PMACETATE)	FLUORAD FC135 1% IN H ₂ O
CC.4	8.19	.40	.02	1.31	.14	.14*A	1.2	.59	.15
IA.4	8.19	1.6	.02	1.31					
CP.4	8.19	.40	.02	1.31	.14				
CA.4	8.19	.40	.02	1.31	.14				

REF	RESIN	H ₂ O	14%NH ₃	BUTYL CELLO- SOLVE	BUTYL CARBITOL	PCD0	FLUORAD FC-135 1% IN H ₂ O
CC.5	77.19	15.44	1.1	4.71	1.57	4.36	1.54
IA.5	77.19	15.44	1.1	4.71	1.57		
(BUTYL CELLOSOLVE is ethylene glycol monobutyl ether sold by Union Carbide. BUTYL CARBITOL is diethylene glycol monobutyl ether sold by Union Carbide. PM ACETATE is propylene glycol monomethylether acetate sold by ICI Americas. FLUORAD is a wetting agent sold by 3M Corp.)							

EXAMPLE C PREPARATION OF COATING FILMS FOR TESTING

[0046] Films of the prepared coating samples were either cast on aluminium panels or sprayed onto wooden panels. For the aluminium panels the films were cast for a 0.0025 cm (1 mil) DFT (dried film thickness). For the wooden panels the films were air sprayed for a 0.0025 cm (1 mil) DFT seal coat and a 0.0025 cm (1 mil) DFT topcoat. The films were typically air dried for 1 week prior to testing. The samples were then tested according to the following established test procedures.

EXAMPLE D TEST PROCEDURESD1. MAR RESISTANCE TEST

5 [0047] This test measures the extent of damage done to an organic coating when it is struck with a finger nail. In this test, panels are coated with samples and then cured. The cured samples are then tested for mar resistance by two methods. The first method ("surface mar") includes striking the coating vigorously several times with the back of a fingernail. The second method ("dig-in mar") includes trying to dig the finger nail into the coating. Each coating is then rated for each method on a scale from 0 to 10 with 10=no mark. The results are reported as two values (x/y) corresponding to ratings for each respective method. An improvement of 1 is an important advantage.

D2. MEK RUB RESISTANCE TEST

15 [0048] This test measures the extent of damage done to a coating on a panel when exposed to methyl ethyl ketone (MEK). In this regard, a cheese cloth is first saturated with MEK. Then, by use of a Crockmeter (Atlas Electric Devices Inc.) the cloth is rubbed on the coating on the panel. In the test, two values (x/y) are recorded. The first is when breakthrough to the panel is first observed. The second is when there has been 80% coating film damage. The data are reported as double rubs (one set of back and forth). The higher the number of rubs, the better the coating film.

D3. SWARD HARDNESS TEST

20 [0049] This test follows the procedure laid down in ASTM designation D 2134-66 (Reapproved 1980), except that the film is not softened with a plasticiser. In short, a weighted wheel rocks like a pendulum on a coating film on a panel. In the test, one measures the number of swings before the motion is dampened by a certain amount. The higher the number of swings, the harder the film.

D4. PENCIL HARDNESS TEST

30 [0050] This test is a rapid and inexpensive determination of the film hardness of an organic coating on a substrate in terms of drawing leads or pencil leads of known hardness. The test is laid out in detail under ASTM designation D 3363-74 (Reapproved 1980). In short, a panel is coated and cured and then tested for pencil hardness using a mechanical holder. Lead of varying hardness was flattened on the end and then pressed against the coating at a 45° angle until either the lead broke or a cut was made through the coating to the substrate. The coating hardness is rated by the hardest lead which does not tear the coating, according to the following chart in order of increasing hardness: 6B, 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H, 7H, 8H.

D5. KNOOP HARDNESS TEST

40 [0051] This test is a measure of the indentation hardness of organic materials such as paint when applied to an acceptable plane rigid surface of a panel. The test is laid out in detail under ASTM designation D 1474-85. In short, a 25 gram load is placed on the dried film by use of a diamond stylus. The indentation left on the film by the diamond stylus is measured under a microscope. The smaller the measured indentation, the harder the coating film.

D6. HOT PRINT TEST

45 [0052] This test measures the hardness of a coating film by measuring the extent of an imprint of a weighted cheese-cloth. In this test, a sample is coated on a panel and cured. A piece of cheesecloth is then placed over the coated side of the panel and held at 60°C. (140°F.) for 4 hours at 1406 kgm⁻² (2 pounds/square inch pressure). The cheesecloth is then removed. The coating is then inspected to see whether there is an imprint of the cheesecloth. The coating is then rated on a scale from 0-10 where 0=can not move the cheese cloth and 10=no printing.

D7. COMPOSITE STAIN TEST

55 [0053] This test measures the extent of staining of a coating film on a panel after being exposed to a stain solution. The stains for the composite stain were water, 50 % EtOH, 1 % Dreft, Formula 409, vinegar and 7% NH₃. The stain agents were in contact with the film for 16 hours and were covered to prevent evaporation. Each stain is done separately and the results averaged. The data is presented as initial rating/rating after 24 hours recovery. The data is recorded on a scale of 0-10 wherein 10 is best.

D8. ACETONE OR DMF SPOT TEST

[0054] This test is similar to the Composite Stain test except that the stain solution is acetone or DMF (dimethylformamide) and the film is exposed for just either 10 minutes or 1 hour. The data are presented showing the two respective values.

The following results show that the aromatic polycarbodiimides according to the present invention display properties, such as mar resistance and MEK rubs, that are both better than the prior art aliphatic polycarbodiimides and at least comparable to the toxic aziridine cross-linkers.

EXAMPLE 1

Substrate: Aluminium

[0055]

SAMPLE:	CC.1	IA.1	CP.1	CA.1
PROPERTY				
Mar Resistance	2/1	5/3	2/1	4/3
MEK Rubs	1/1	10/15	2/3	25/35
Pencil Hardness	3B	B	B	HB
Sward Hardness	10	25	18	15

EXAMPLE 2

Substrate: Aluminium

[0056]

SAMPLE:	CC.2	IA.2	CP.2	CA.2
PROPERTY				
Mar Resistance	1/1	4/3	GELLED	4/3
MEK Rubs	2/2	5/10	GELLED	30/80
Sward Hardness	22	34	GELLED	32
Knoop Hardness	0.9	5.2	GELLED	2.0

EXAMPLE 3

Substrate: Aluminium

[0057]

SAMPLE:	CC.3	IA.3	CA.3
PROPERTY			
Mar Resistance	2/1	5/4	6/5
MEK Rubs	5/5	35/60	>500/>500
Sward Hardness	55	56	55
Knoop Hardness	4.6	8.4	9.5
Hot Print	1	5	8
Composite Stains	0/1	4.5/5	7.5/9

EXAMPLE 4

Substrate: Aluminium

5 [0058]

10

SAMPLE:	CC.4	IA.4	CP.4	CA.4
PROPERTY				
Mar Resistance	3/2	4/3	2/1	4/3
MEK Rubs	5/5	25/60	10/25	150/>500
Hot Print	2	4	3	4

EXAMPLE 5

15

Substrate: Cherry Veneer

[0059]

20

25

SAMPLE:	CC.5	IA.5
PROPERTY		
Mar Resistance	3/2	4/4
Hot Print	4	7
Composite Stains	2/5.5	7/8
10 min AST	7/6	8/8
1 hr AST	4/4	7/7
(AST = Acetone Spot Test)		

30

EXAMPLE 6. Cross-linking polyurethane dispersion with aromatic carbodiimide

[0060] Coating compositions containing an polyurethane dispersion bearing at least two carboxylic acid groups were prepared by adding the ingredients presented in Table 6.1 with mixing, in the order given

35

Table 6.1

40

45

50

Preparation of polyurethane dispersion compositions				
Coating composition:	6-1	6-2	6-3	6-4
Polyurethane dispersion (SANCURE 825)	25.0	25.0	25.0	25.0
Water	1.5	9.1	3.05	-
Aziridine (XAMA-7)	0.75	-	-	-
Aliphatic carbodiimide (UCARLINK XL-29SE)	-	4.1	-	-
Aromatic polycarbodiimide - (EXAMPLE A.5)	-	-	3.05	-

[0061] Coating compositions 6-1 to 6-4 were drawn down on an Aluminum panel at a dry film thickness of 1 mil and air-dried. Test results are presented in Table 6.2

[0062] Table 6.2 Testing of cured polyurethane dispersion compositions

55

Coating composition:	6-1	6-2	6-3	6-4
Sward Hardness	28	-	29	28

(continued)

1 hr. AST	8/8	6/7	8/8	7/7
1 hr. DMF spot test	8/10	1/1	8/9	2/3
Composite stain test	5/8	3/8	5/9	3/5

[0063] Coating composition 6-3 of this invention exhibits cured coating properties superior to the uncured dispersion (6-4); and improved coating properties on balance relative to comparative coatings 6-1 and 6-2.

[0064] EXAMPLE 7. Cross-linking a styrenated acrylic latex with an aromatic carbodiimide for use as an exterior hardboard primer.

[0065] An exterior primer was prepared by blending with mild agitation 5.29 g. of triethylamine-neutralized acrylic pigment dispersant (23.7% solids ACRY SOL I -62; ACRY SOL is a trademark of Rohm and Haas Co., 12.5 g. deionized water, and 0.45 g. defoamer (BALAB 3056A; BALAB is a trademark of Witco Chem. Co.). The mixture was then poured into a Cowles dispersed with strong agitation. The following pigments were then mixed in: 10. g. titanium dioxide (TIPURE R-960; TIPURE is a trademark of Dupont Corp.), 44.2 g. silica (NEOSIL A; NEOSIL is a trademark of Tammco Co.), 4 g. clay (ASP-400; Englehard Co.), 0.1 g. bentonite (BENTON LT; BENTON is a trademark of NL Industries, and 0.1 g. Aurasperse W-7012 (Harshaw Corp.). The fineness of grind was measured to be 6-7 Hegman. The resulting mixture was then blended with 49.7 g. styrenated acrylic latex bearing at least two carboxylic acid groups (45.2% solids; polymer containing 8% methacrylic acid), 12.7 g. aromatic carbodiimide (50% solids; Example A.5), 0.6 g. rheology modifier (ACRY SOL RM-825; ACRY SOL is a trademark of Rohm and Haas Co.), and 18.4 g. deionized water.

[0066] The coating composition was applied on X-90 hardboard (composite wood product of Masonite Corp.) at a wet thickness of 8 mils and cured for 2.5 min. at room temperature, then 3.0 min. at 300° F.(149 C.), and then 3.5 min. at 405° F.(207 C.) in a convection oven. The board surface temperature immediately on removal from the oven was 325° F.(163 C.) The coating was tested and had 178 MEK rubs and good block resistance with no wax migration.

[0067] EXAMPLE 8. Crosslinking an acrylic latex with an aromatic carbodiimide for use as a binder for a nonwoven fabric.

[0068] Preparation of Sample 8. To 152.6 g. acrylic latex bearing at least two carboxylic acid groups (48.2 ethyl acrylate/48.2 butyl acrylate/3.6 methacrylic acid) was added 328 g. water and 4.6 g. ammonia. Then 4.75 g. aromatic polycarbodiimide (50% solids content; Example A.5) was diluted with 10 g. water and stirred into the diluted latex. The final formulation solids content of the binder composition was 9%. A comparative sample was prepared except for the deletion of the aromatic polycarbodiimide.

[0069] A DACRON 730W (DACRON is a trademark of DuPont Co.) polyester nonwoven, 1.5 denier, 1.5 inch staple length, merge 613-D3H, nonwoven web, nominally 1 oz./sq. yd. (40.6 g./m²), thermally pre-bonded was used for tensile test and drape flex testing. A carded nonwoven web of DACRON 371W fibres, nominally 1 oz./sq. yd. which was not heat bonded was used for wash durability and dryclean testing. Webs were supported between fiberglass scrim, saturated with the binder composition, and passed through a Birch Bros. padder at 40 psig (2828 mm.Hg). The fiberglass scrim was removed and each web placed in a Mathis oven at 150 C. for 5 min. to dry and cure the binder composition.

[0070] Tensile Testing. Samples were tested dry and wet after soaking for 30 min. in a 0.1% TRITON X-100 (TRITON is a trademark of Union Carbide Corp.) solution in water ("water-wet"), isopropanol, or perchloroethylene (DOWPER CS; DOWPER is a trademark of Dow Chemical Co. ("perchlor-wet"). For each evaluation, as presented in Table 8.1, five samples were cut from each of two replicate webs and the average reported.

Table 8.1

Tensile testing of nonwoven webs containing acrylic binder crosslinked with aromatic polycarbodiimide.				
Sample	Tensile Strength (g./in.) (g/cm)			
	Dry	Water-wet	Isopropanol wet	Perchlor-wet
8	2009(791)	1327(522)	671(264)	707(278)
Comparative	1010(398)	501(197)	too weak	too weak

[0071] Wash Durability. Samples of bonded nonwoven 9 inches (23 cm.) by 10 inches (25.5 cm.) were cut from the web which had not been thermally prebonded. They were washed in a home washing machine, full cycle wash, "hot" (50-60 C.) water, ½ cup of TIDE ULTRA powder (TIDE is a trademark of Procter and Gamble), and eight terry cloth towels. At the end of each cycle, fabrics were examined and were rated as failed if they had split into more than one piece or had roped. Results are presented in Table 8.2.

[0072] Fabric Stiffness. ASTM D 1388 Stiffness of Fabrics, Option A - Cantilever Test (Drape Flex), FRL Cantilever Bending Tester (Testing Machines Inc., Amityville, N.Y., motor-driven, constant rate, was used. The average of six

samples bent across fabric machine direction is reported in Table 8.2

Table 8.2

Wash and Drape-flex testing of nonwoven webs containing acrylic binder crosslinked with aromatic polycarbodiimide.		
Sample		
	Washes Survived	Drape-flex(mm.)
8	>85	87
Comparative	11	72

[0073] Sample 8 of this invention exhibits superior performance as a nonwoven fabric binder relative to the comparative sample.

[0074] **EXAMPLE 9.** Crosslinking an acrylic latex with an aromatic carbodiimide for use as a binder for a leather basecoat.

[0075] Preparation of Comparative 9. To 59 g. of an acrylic emulsion polymer bearing at least two carboxylic acid groups was added 12 g. of a clay dispersion (LA Neutral from Rohm and Haas Co.), 8 g. of a wax dispersion (PRIMAL C-7; PRIMAL is a trademark of Rohm and Haas Co.), and 21 g. of a pigment dispersion (LA Black P from Rohm and Haas Co.).

[0076] Preparation of Samples 9-1 and 9-2. Aromatic polycarbodiimide (Example A.5) was added to the acrylic emulsion of Comparative 9 and mixed well before adding the other ingredients. In sample 9-1, 3.5 phr. aromatic polycarbodiimide was used; in sample 9-2, 7.0 phr. aromatic polycarbodiimide was used.

[0077] Comparative 9 and Samples 9-1 and 9-2 were sprayed onto split leather using a pressurized air spray gun.

[0078] Embossing. Embossing using a heated press at 110 C. was used to imprint patterns into the coated leather. A tendency of the coated leather to cling to the opened press is rated; clinging is undesirable. Results are presented in Table 9.1

[0079] Bally Flex Test. The wet Bally flex test evaluates the ability of the coated leather to remain flexible while resisting the tendency of the leather fibers to punch through the finish from underneath. A dry Bally flex test is also run to evaluate the flexibility of the coating. Coated samples are run for 100,000 flexes, wet or dry. Results are presented in Table 9.1.

[0080] Block Test. The blocking tendency is evaluated on coating to coating contact for 1 hour at 275 F.(121°C.) under a 500 gram load. Results are presented in Table 9.1

Table 9.1

Testing of base-coated leather			
	Comp. 9	Sample 9-1	Sample 9-2
Embossing (plate cling)	moderate	very slight	none
Wet Bally Flex Appearance	sl. pinholes	no damage	no damage
Dry Bally Flex Appearance	sl. cracks	no damage	few cracks
Block Test (cling)	severe	moderate	slight

[0081] Samples 9-1 and 9-2 of this invention exhibited superior performance as crosslinked coating binders for leather basecoats relative to comparative 9.

EXAMPLE 10. Crosslinking an acrylic/polyurethane blend with an aromatic carbodiimide for use as a binder for a leather topcoat.

[0082] Preparation of Comparative 10. To 120 g. water are added with mixing 50 g. ethylene glycol monobutyl ether, 30 g. of a levelling/flow agent (MA-65 from Rohm and Haas Co), 210 g. of an aqueous silica dispersion (PRIMAL Duller 6; PRIMAL is a trademark of Rohm and Haas Co.), 572 g. of a 71/29 blend of an acrylic emulsion polymer/polyurethane dispersion blend, each polymer bearing at least two carboxylic acid groups, 20 g. of a silicone emulsion (LA-2229 from Rohm and Haas Co.), and 45 g. of a thickener (ACRYSOL RM-1020; Acrysol is a trademark of Rohm and Haas Co.).

[0083] Preparation of Sample 10-1. To Comparative 10 was added 50 g. of aromatic polycarbodiimide (Example A.5) last, with mechanical mixing.

[0084] Comparative 10 and Sample 10-1 were sprayed onto basecoated leather using a pressurized air spray gun.

The topcoated leather was dried at 120F for 5 minutes and then cured at room temperature for 16 hours. Prior to testing, after 12 hours, the topcoated leather was milled for 4 hours.

[0085] Wet Veslic Test. The Veslic testing machine (wet pad, 1 kg. load, cyclical rubbing action) was used to evaluate the water resistance of the topcoated leather. Data are presented in Table 10.1

Table 10.1 Testing of topcoated leather

Sample:	<u>Comparative 10</u>	•	<u>Sample 10-1</u>
Wet Veslic Rating	267 cycles; 10% damage		1000 cycles; no damage

Sample 10-1 of this invention exhibited superior performance as a crosslinked coating binder for leather topcoats relative to comparative 10.

EXAMPLE 11. Crosslinking an polyurethane dispersion with an aromatic carbodiimide for use as a binder for a leather topcoat.

[0086] Preparation of Comparative 11. A polyurethane dispersion polymer bearing at least two carboxylic acid groups, water, thickener and flow aids was used as a clear leather topcoat.

[0087] Preparation of Samples 11-1 and 11-2. To Comparative 11 was added 1.5%, based on polyurethane solids (Sample 11-1) or 3%, based on polyurethane solids (Sample 11-2) aromatic polycarbodiimide (Example A.5) last, with mechanical mixing before, during, and after the addition.

[0088] Comparative 101 and Samples 11-1 and 11-2 were sprayed onto basecoated leather using a pressurized air spray gun. The topcoated leather was dried at 120F (49 C.) for 5 minutes and then cured at room temperature for 24 hours.

[0089] Toothill Scuff Test. Scuff resistance of the topcoated leather was rated after 1000 cycles using the Toothill Scuff Tester.

[0090] Wet Veslic Test. As in Example 10

[0091] Block Test. Conditions were 300 F/2 psi./1 hour (149 C./103mm.Hg./1 hour)

[0092] Wet Crock Test. Cycles passed using an AATCC Crockmeter with a 4 lb. (1.81 Kg) load.

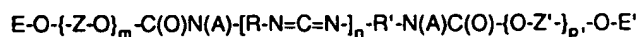
Table 11.1

Testing of topcoated leather			
	Comp. 11	Sample 11-1	Sample 11-2
Block Test(cling)	severe 100% damage	moderate 60% damage	moderate+ 70% damage
Toothill Scuff Test	poor	fair	fair
Wet Veslic Rating	115 cycles	155 cycles	125 cycles
Wet Crock Test	60 cycles	350 cycles	170 cycles

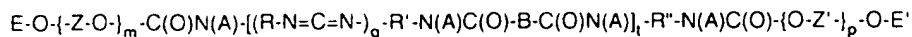
[0093] Samples 11-1 and 11-2 of this invention exhibited superior performance as crosslinked polyurethane coating binders for leather topcoats relative to Comparative 11.

Claims

1. An aromatic polycarbodiimide, useful in a method of crosslinking a coating binder polymer bearing at least two carboxylic acid groups, having the general formula of either



or



wherein

m is an integer of from 1 to 15; n is an integer of from 2 to 15; p is an integer of from 1. to 15; q is an integer of from 1. to 15; t is an integer of from 1. to 15;

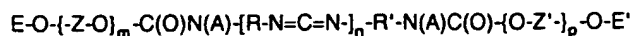
A is independently selected from hydrogen or C1-C6; B being an ether or ester spacer group which does not contain carbodiimide groups; E and E' are hydrogen or C1-C10 alkyl and may be the same or different; R, R' and R'' are independently selected from arylene, substituted arylene, biarylene alkylene and substituted biarylene alkylene; and Z and Z' C1-C6 alkylene groups,

and may be the same or different; and where the aromatic carbodiimide does not contain a chemically incorporated sulfonate group.

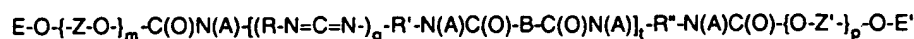
2. An aromatic polycarbodiimide as claimed in claim 1 wherein m is an integer of from 1 to 10; n is an integer of from 2 to 10; p is an integer of from 1 to 10; q is an integer of from 1 to 10; t is an integer of from 1 to 10; A is independently selected from hydrogen or C1 to C6 alkyl; B is an ether or ester spacer group not containing carbodiimide groups, E and E' are hydrogen or a C1 to C10 alkyl group and may be the same or different; R, R' and R'' are independently selected from arylene, substituted arylene, biarylene alkylene and substituted biarylene alkylene groups, and Z and Z' are C1-C6 alkylene groups, and may be the same or different.
3. A method of cross-linking a coating binder bearing at least two carboxylic acid groups, the method comprising admixing a polycarbodiimide with the coating binder polymer, characterized in that the polycarbodiimide is an aromatic polycarbodiimide as claimed in claim 1 or claim 2.
4. The method of claim 3, wherein the coating binder polymer is or is in a water-borne coating formulation.
5. The method claims 3 or 4, wherein the coating binder polymer is a polyurethane dispersion.
6. The method of claims 2, 3, 4, or 5, wherein the coating binder polymer has an acid number from 5 to 100.
7. Use of an aromatic polycarbodiimide as defined in claim 1 or claim 2 as a crosslinker for a coating binder polymer bearing at least two carboxylic acid groups.
8. A composition comprising the aromatic polycarbodiimide of claim 1 or claim 2 having a reduced tendency to thicken with time, the composition further comprising a stabilizer selected from the group consisting of 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propanoate)methane, 2,4-dimethyl-6-tert-butyl phenol, 4-hydroxy-2,2,6,6-tetramethylpiperidiny-1-oxyl, and mixtures thereof.
9. A substrate bearing a crosslinked polymer prepared by any one of claims 3 to 6; the substrate being selected from the group consisting of wood, leather, and nonwoven fabrics

Patentansprüche

1. Ein aromatisches Polycarbodiimid, das in einem Verfahren zur Vernetzung eines Beschichtungsbindemittelpolymer, das mindestens zwei Carbonsäuregruppen trägt, nützlich ist, mit der allgemeinen Formel



oder



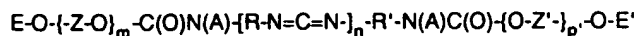
worin

m eine ganze Zahl zwischen 1 und 15 ist; n eine ganze Zahl zwischen 2 und 15 ist;
 p eine ganze Zahl zwischen 1 und 15 ist; q eine ganze Zahl zwischen 1 und 15 ist;
 t eine ganze Zahl zwischen 1 und 15 ist; A unabhängig ausgewählt ist aus Wasserstoff oder C1-C6; B eine
 Ether- oder Esterspacergruppe ist, die keine Carbodiimidgruppen enthält; E und E' Wasserstoff oder
 C1-C10-Alkyl sind und gleich oder verschieden sein können; R, R' und R'' unabhängig voneinander ausgewählt
 sind aus Arylen, substituiertem Arylen, Biarylenalkylen und substituiertem Biarylenalkylen; und Z und Z'
 C1-C6-Alkylengruppen sind und gleich oder verschieden sein können; und worin das aromatische Carbodiimid
 keine chemisch eingebaute Sulfonatgruppe enthält.

2. Ein aromatisches Polycarbodiimid gemäß Anspruch 1, worin m eine ganze Zahl zwischen 1 und 10 ist; n eine
 ganze Zahl zwischen 2 und 10 ist; p eine ganze Zahl zwischen 1 und 10 ist; q eine ganze Zahl zwischen 1 und 10
 ist; t eine ganze Zahl zwischen 1 und 10 ist; A unabhängig ausgewählt ist aus Wasserstoff oder
 C1-C6-Alkyl; B eine Ether- oder Esterspacergruppe ist, die keine Carbodiimidgruppen enthält, E und E' Wasserstoff
 oder eine C1-C10-Alkylgruppe sind und gleich oder verschieden sein können; R, R' und R'' unabhängig vonein-
 ander ausgewählt sind aus Arylen-, substituierten Arylen-, Biarylenalkylen- und substituierten Biarylenalkylen-
 Gruppen, und Z und Z' C1-C6-Alkylengruppen sind und gleich oder verschieden sein können.
3. Ein Verfahren zur Vernetzung eines Beschichtungsbindemittels, das mindestens zwei Carbonsäuregruppen be-
 trägt, wobei das Verfahren das Beimischen eines Polycarbodiimids mit dem Beschichtungsbindemittelpolymer
 umfaßt, dadurch gekennzeichnet, daß das Polycarbodiimid ein aromatisches Polycarbodiimid gemäß Anspruch 1
 oder Anspruch 2 ist.
4. Das Verfahren nach Anspruch 3, worin das Beschichtungsbindemittelpolymer eine wasserlösliche Beschichtungs-
 formulierung ist oder in einer wasserlöslichen Beschichtungsformulierung vorliegt.
5. Das Verfahren nach Anspruch 3 oder 4, worin das Beschichtungsbindemittelpolymer eine Polyurethan-Dispersion
 ist.
6. Das Verfahren nach Anspruch 2, 3, 4 oder 5, worin das Beschichtungsbindemittelpolymer eine Säurezahl zwischen
 5 und 100 hat.
7. Verwendung eines aromatischen Polycarbodiimids gemäß Anspruch 1 oder Anspruch 2 als Vernetzungsmittel für
 ein Beschichtungsbindemittelpolymer, das mindestens zwei Carbonsäuregruppen trägt.
8. Eine Zusammensetzung, umfassend das aromatische Polycarbodiimid nach Anspruch 1 oder Anspruch 2, welche
 eine verringerte Neigung aufweist, mit der Zeit einzudicken, wobei die Zusammensetzung weiter umfaßt einen
 Stabilisator, ausgewählt aus der Gruppe, bestehend aus 3-(3',5'-Di-tert-butyl-4'-hydroxyphenyl)propanat)methan,
 2,4-Dimethyl-6-t-butylphenol, 4-Hydroxy-2,2,6,6,-tetramethylpiperidinyl-1-oxy und Gemischen davon.
9. Ein Substrat, das ein vernetztes, nach einem der Ansprüche 3 bis 6 hergestelltes Polymer trägt, wobei das Substrat
 aus der Gruppe, bestehend aus Holz, Leder und Vliesstoffen, ausgewählt ist.

Revendications

1. Polycarbodiimide aromatique, utile dans un procédé de réticulation d'un polymère, liant de revêtement, portant au
 moins deux groupes acide carboxylique, répondant à la formule générale



ou



- formules dans lesquelles m est un nombre entier de 1 à 15 ; n est un nombre entier de 2 à 15 ; p est un nombre entier de 1 à 15 ; q est un nombre entier de 1 à 15 ; t est un nombre entier de 1 à 15 ; A est choisi indépendamment parmi un atome d'hydrogène ou un groupe en C₁-C₆ ; B étant un groupe écarteur éther ou ester qui ne contient pas de groupes carbodiimide ; E et E' sont des atomes d'hydrogène ou des groupes alkyle en C₁-C₁₀ et peuvent être identiques ou différents ; R, R' et R" sont choisis indépendamment parmi les groupes arylène, arylène substitué, biarylène-alkylène et biarylène-alkylène substitué ; et Z et Z' sont des groupes alkylène en C₁-C₆ et peuvent être identiques ou différents ; et dans lesquelles le polycarbodiimide aromatique ne contient pas de groupe sulfonate incorporé dans la structure chimique.
2. Polycarbodiimide aromatique selon la revendication 1, dans lequel m est un nombre entier de 1 à 10 ; n est un nombre entier de 2 à 10 ; p est un nombre entier de 1 à 10 ; q est un nombre entier de 1 à 10 ; t est un nombre entier de 1 à 10 ; A est choisi indépendamment parmi un atome d'hydrogène ou un groupe alkyle en C₁-C₆ ; B est un groupe écarteur éther ou ester qui ne contient pas de groupes carbodiimide ; E et E' sont des atomes d'hydrogène ou des groupes alkyle en C₁-C₁₀ et peuvent être identiques ou différents ; R, R' et R" sont choisis indépendamment parmi les groupes arylène, arylène substitué, biarylène-alkylène et biarylène-alkylène substitué ; et Z et Z' sont des groupes alkylène en C₁-C₆ et peuvent être identiques ou différents.
 3. Procédé de réticulation d'un liant de revêtement portant au moins deux groupes acide carboxylique, le procédé comprenant le mélange d'un polycarbodiimide avec le polymère liant de revêtement, caractérisé en ce que le polycarbodiimide est un polycarbodiimide aromatique selon la revendication 1 ou 2.
 4. Procédé selon la revendication 3, dans lequel le polymère liant de revêtement est une formulation de revêtement diluable à l'eau ou est contenu dans une telle formulation.
 5. Procédé selon la revendication 3 ou 4, dans lequel le polymère liant de revêtement est une dispersion de polyuréthane.
 6. Procédé selon les revendications 2, 3, 4 ou 5, dans lequel le polymère liant de revêtement possède un indice d'acide de 5 à 100.
 7. Utilisation d'un polycarbodiimide aromatique tel que défini dans la revendication 1 ou la revendication 2 en tant qu'agent de réticulation pour un polymère liant de revêtement portant au moins deux groupes acide carboxylique.
 8. Composition comprenant le polycarbodiimide aromatique selon la revendication 1 ou la revendication 2, ayant une tendance réduite à s'épaissir avec le temps, la composition comprenant par ailleurs un stabilisant choisi dans le groupe constitué par le 3-(3',5'-di-tert-butyl-4'-hydroxyphényl)propionate)méthane, le 2,4-diméthyl-6-t-butylphénol, le 4-hydroxy-2,2,6,6-tétraméthylpipéridinyl-1-oxy, et leurs mélanges.
 9. Substrat portant un polymère réticulé préparé selon l'une quelconque des revendications 3 à 6, le substrat étant choisi dans le groupe constitué par le bois, le cuir et les tissus non tissés.